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Organic Conductors

X-Ray Absorption Edge Studies in HMTSeF,  
(HMTSeF)(TCNQ) and (HMTSeF)(TCNQF<sub>4</sub>). P.M. GRANT,  
W.D. GILL, H. MORAWITZ, K. BECHGAARD,† and D.L. SAYERS,\*  
IBM Research Lab.--We have measured the Se K<sub>α</sub> absorp-  
tion edge spectrum in HMTSeF, (HMTSeF)(TCNQ) and  
(HMTSeF)(TCNQF<sub>4</sub>). The charge transfer state of the  
HMTSeF molecule in these three compounds is believed to  
be 0, 0.74 and 1, respectively. HMTSeF and (HMTSeF)  
(TCNQF<sub>4</sub>) are insulating while (HMTSeF)(TCNQ) has the  
highest room temperature conductivity of known TCNQ  
salts. If the net charge transfer state in (HMTSeF)  
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buted neutral and ionic molecular species, as opposed  
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plest model for the Se x-ray absorption in the cation  
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position of the spectra resulting from HMTSeF and  
(HMTSeF)(TCNQF<sub>4</sub>). This does not appear to be the re-  
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simple picture.

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- ( ) Prefer Poster Session
- (x) Prefer Standard Session
- ( ) No preference

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In the SeCN case, the three-dimensional ordering of the charge density waves below  $T_0 = (175 \pm 5)K$  drives a tetragonal to monoclinic structural transition, rather than simply an increase in the monoclinic angle as in SCN. In the TCNQ compound, the angle  $\beta$  exhibits a small deviation ( $\leq 0.04^\circ$ ), for temperatures near 38 K to 47 K, from the smooth variation of the lattice constants a, b and c.

**AE 11 Structural, Electrical and Spectral Studies of Several Members of the Class of Conductive Low-Dimensional Materials--TTF $\cdot$ I $_x$** , T.J. MARKS, R.C. TEITELBAUM, M.S. McCLURE, C.R. KANNENWURF, Northwestern U.\*; C.K. JOHNSON, Oak Ridge Nat. Lab.†, and S.L. RUBY, Argonne Nat. Lab.†--The organic donor tetrathiafulvalene, TTF, forms a number of highly conductive phases with iodine. Identification of the form of iodine present (i.e. I $^-$ , I $_2$ , I $_3^-$ , I $_5^-$  or mixtures thereof) allows a direct measurement of the degree of partial oxidation (incomplete charge transfer) in these materials. We report here comparative resonance Raman, X-ray crystallographic, and iodine-129 Mössbauer studies on the materials TTF $\cdot$ I $_{0.71}$ , two forms of TTF $\cdot$ I $_2$  (one new, triclinic), and TTF $\cdot$ I $_3$  (new, monoclinic) which reveal donor-acceptor orientations and the degree to which the stacked TTF molecules have been oxidized. We also report variable temperature four-probe electrical conductivity measurements.

\*Supported in part by the NSF-MRL program under grant No. DMR 76-80847 and in part by the Office of Naval Research

†Supported by the Department of Energy

**AE 12 Seebeck Coefficients of TTF C $_x$ .67**\* TIMIR DATTA, R. J. DECK, A. M. HERMANN, Tulane University; R. B. SOMOANO, Jet Propulsion Laboratory--The Seebeck coefficient of TTF C $_x$ .67 will be reported. The observed room temperature value (+6.5  $\mu$ V/K) is relatively insensitive to temperature above 230 K, below which temperature it becomes large and remains positive. The high temperature value is considerably larger than that reported previously for TTF C $_x$ .70, + 0.5  $\mu$ V/K. These findings will be discussed in comparison with thermoelectric data of other TTF halides and pseudohalides.

\*Supported in part by JPL Contract No. NAS-7-100, sponsored by NASA

**AE 13 Optical Properties as a Function of Band Filling: (NMP) $_x$ (Phen) $_{1-x}$ (TCNQ)**, 0.5 < x < 1.0. B.A. WEINSTEIN, M.L. SLADE, AND A.J. EPSTEIN, Xerox Webster Research Center, N.Y. 14580; J.S. MILLER Rockwell Int., Calif. 91360. -- We have measured the room temperature polarized reflectivity of single crystals of this isomorphous series of materials from 1.5 eV to .2 eV. A Drude-like edge is observed for light polarized parallel to the TCNQ stacking (a-) axis. For X = 1.0 our results agree with the previous work of Wrighton et al. on (NMP)(TCNQ). For increasing phenazine concentration this edge is observed to shift to lower energy, consistent with decreasing band filling (charge transfer). There is no Drude-like edge for light polarized perpendicular to the a-axis, although a molecular mode at .37 eV, presumably associated with the presence of phenazine, becomes apparent for X < 1.0.

**AE 14 ELECTRON SPIN RESONANCE PROPERTIES AS A FUNCTION OF BAND FILLING: (NMP) $_x$ (Phen) $_{1-x}$ (TCNQ)**, 0.5 < x < 1.0. A.P. TROUP and A.J. EPSTEIN, Xerox Corporation, Webster Research Center, Webster, N.Y. 14580 and J.S. MILLER, Rockwell Int. Science Ctr., Thousand Oaks, CA 91360--We have measured the temperature dependence of the ESR signal of single crystals of this isomorphous series of materials for 6K < T < 300K. Linewidths, g-values and microwave susceptibility are examined as a function of T and x. The linewidth increased with phenazine doping while g(T) appears relatively

insensitive to x for large x. The microwave susceptibility varies as T $^{-\gamma}$  ( $\gamma \sim 0.8-0.9$ ) for T < 40K, in agreement with dc susceptibility. Comparison with the dc susceptibility and other experiments and models will be presented.

**AE 15 Magnetic Susceptibility Studies in a System with Varying Disorder and Charge Transfer: (NMP) $_x$ (Phen) $_{1-x}$ (TCNQ)**, 0.5  $\leq$  x  $\leq$  1.0. A. J. EPSTEIN, Xerox Webster Research Center, Rochester, N. Y. 14644, and J. S. MILLER, Rockwell Int. Science Center, Thousand Oaks, Calif. 91360.--Detailed studies of the dc magnetic susceptibility of this isomorphous series is reported. Measurements were made over a temperature range of 1.8K to 320K and for magnetic fields of up to 80K Oe. Below 30K, the susceptibility,  $\chi$ , increases with decreasing temperature, T, as  $\chi = AT^{-\gamma}$ , with A and  $\gamma$  constant. This interpreted as the contribution of a few percent of localized spins with a probability distribution of exchange of the form P(J)  $\propto$  J $^{-\gamma}$ . The exponent  $\gamma$  is found to be only weakly sample and x dependent, demonstrating that large changes in the degree of disorder have little effect on this behavior. The prefactor A decreases with initial phenazine doping consistent with the replacement of radical NMP $^{\cdot-}$  molecules with spinless Phen $^0$ . Other chemical possibilities will be discussed. Data for T > 30K are discussed in terms of large coulomb interactions among delocalized electrons. These results are consistent with transport studies in this system.

**AE 16 Attempts to Observe Minimum Metallic Conductivity in "1-D" Conductors.** G. J. Dolan, D. D. Osheroff and D. C. Tsui, Bell Laboratories, Murray Hill, N.J.--According to recent theoretical arguments by D. Thouless, any long, narrow conductor will show an increase in resistance at sufficiently low temperatures (becoming an insulator at T=0K) so long as its nominal resistance exceeds  $r = \frac{2\hbar}{e^2} \approx 4000\Omega$ . (1) In an effort to verify Thouless' hypothesis we have made resistance measurements on evaporated thin film "wires" of Au and Au $_{58}$ Pd $_{42}$  and on Silicon Mosfets with long, narrow gate electrodes down to temperatures as low as 10 mK. Null results have been obtained on specimens easily satisfying Thouless' criteria for observation. However, as yet unexplained temperature dependent increases in the zero bias resistance of some very thin, high resistance thin film "wires" ( $r \sim 6M\Omega$ , greatly exceeding the Thouless requirement) suggest that further study of such systems is desirable.

1. D. Thouless, Phys. Rev. Letters **39**, 1168 (1977).

#### Supplementary Program

**AE 17 X-Ray Absorption Edge Studies in HMTSeF, (HMTSeF)(TCNQ) and (HMTSeF)(TCNQF $_4$ )**. P.M. GRANT, W.D. GILL, H. MORAWITZ, K. BECHGAARD,† and D.L. SAYERS,\* IBM Research Lab.--We have measured the Se K $_{\alpha}$  absorption edge spectrum in HMTSeF, (HMTSeF)(TCNQ) and (HMTSeF)(TCNQF $_4$ ). The charge transfer state of the HMTSeF molecule in these three compounds is believed to be 0, 0.74 and 1, respectively. HMTSeF and (HMTSeF)(TCNQF $_4$ ) are insulating while (HMTSeF)(TCNQ) has the highest room temperature conductivity of known TCNQ salts. If the net charge transfer state in (HMTSeF)(TCNQ) were to arise from a Wigner lattice of distributed neutral and ionic molecular species, as opposed to a uniform continuous charge distribution, the simplest model for the Se x-ray absorption in the cation would suggest its spectrum should be a weighted superposition of the spectra resulting from HMTSeF and (HMTSeF)(TCNQF $_4$ ). This does not appear to be the result. We will discuss the effects of excited state lifetime and relaxation which complicate the above simple picture.

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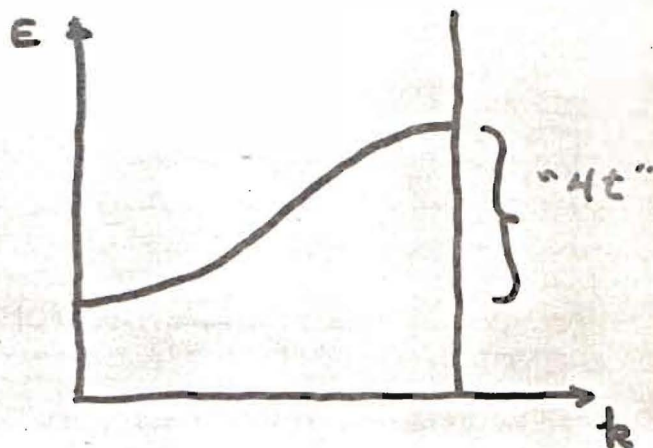
## Outline of AE17: HMTSeF X-ray Absorption

- Introduction
  - Wigner lattice vs delocalization
  - Use of core-level spectroscopy to answer this issue
  - X-ray absorption: advantages over XPS, bulk experiment
- Swingle, et al XPS Data
- Crystalline Se and  $\text{SeO}_2$  data show sensitivity to surroundings
- Compare crystalline Se to HMTSeF and show charge transfer appears in neutral molecule
- Data of the three materials
- Fit to these data: how oscillator strengths shift
- Synthetic attempt to create (HMTSeF)(TCNQ) from spectral superposition of HMTSeF and (HMTSeF)(TCNQF<sub>4</sub>)
- Conclusion
  - Cannot interpret source of individual peaks, but using spectral superposition can show delocalized final state most probable.

## WIGNER - LATTICE



## BAUD PICTURE



## - CORE LEVEL SPECTROSCOPY

- XPS

- XRA

## - ADVANTAGES OF XRA

- BULK EXPERIMENT

- WEAKER "RELAXATION" EFFECTS

- "FINAL STATE" SENSITIVITY

-  $\text{HMTSeF}^\circ$ ,  $(\text{HMTSeF})(\text{TCNQ})$ ,  $(\text{HMTSeF})(\text{TCNQF}_4)$



XPS

GROBMAN, et al.

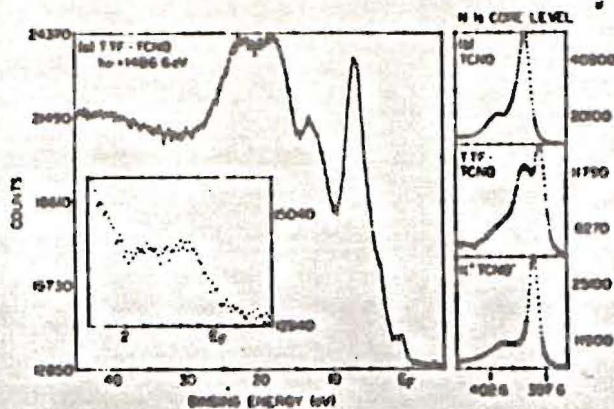


FIG. 2. (a) The x-ray photoemission spectrum ( $h\nu = 1486.6$  eV) of the TTF-TCNQ valence bands ( $\sim 35$  eV wide) and of the highest-lying orbitals (inset).  $E_F$  is determined to  $\sim \pm 0.1$  eV. (b) N-1s core-level spectra for neutral TCNQ, TTF-TCNQ, and  $K^+(TCNQ)^-$ .

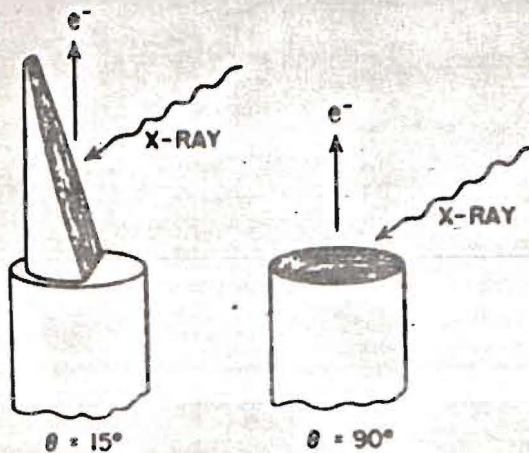


FIG. 1. Sample configuration for grazing-angle experiments.

Swartz, et al.

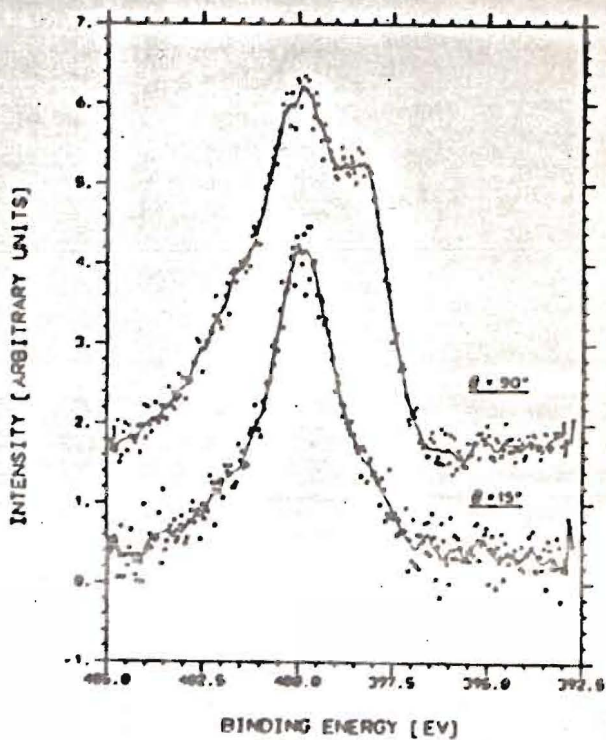


FIG. 2.  $N_{1s}$  grazing-angle spectra for TTF-TCNQ.

RITSKO, et al.

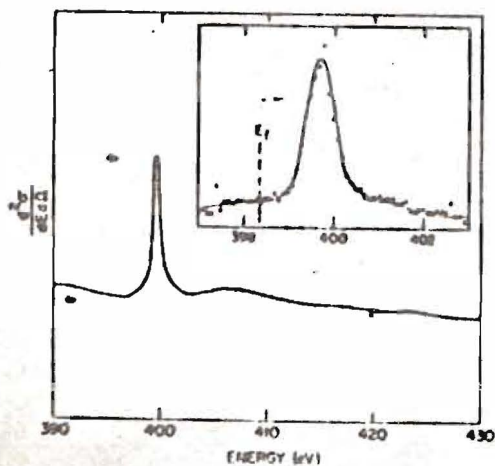


FIG. 2. Inelastic electron scattering spectra above the nitrogen K threshold.

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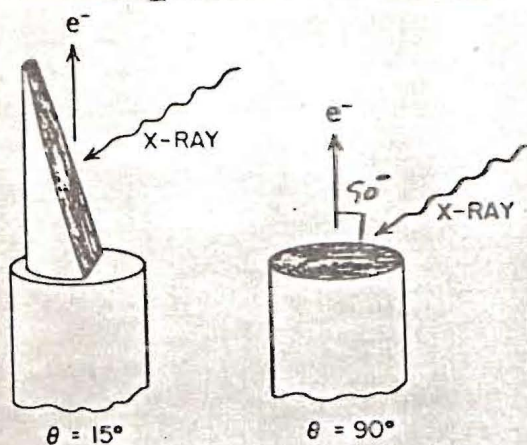


FIG. 1. Sample configuration for grazing-angle experiments.

complex, distinguishable from the bulk material, at the  $a$ - $b$  surface. Empirical evidence indicates this surface layer is characteristic of "good" organic conductors. Of the 24 organic conductor candidates examined, only one (TTF-TCNQ) which showed clear evidence of the surface layer gave a powder-compaction resistivity greater than  $1 \Omega \text{ cm}$ .

For samples with specular surfaces, it is possible to decrease the effective sampling depth by lowering the electron take-off angle,  $\theta$ , between the electron-analyzer entrance and the plane of the sample surface. Grazing-angle spectra for TTF-TCNQ were taken on a DuPont 650B electron spectrometer by mounting 20–50 solution-grown crystals<sup>5</sup> on stubs specially machined for  $90^\circ$  and  $15^\circ$  take-off angles (see Fig. 1). The crystals were closely packed so as to cover the entire surface of the holder and were aligned with their needle axis parallel to one another ( $a$ - $b$  plane exposed). Other compounds, prepared by literature procedures,<sup>7,8</sup> were studied as powders using a Varian IEE-15 spectrometer and an instrument previously described.<sup>9,10</sup> An analog curve resolver was used to deconvolute overlapping peaks.

Figure 2 compares typical background corrected  $N_{1s}$  spectra from TTF-TCNQ taken at  $\theta = 90^\circ$  and  $\theta = 15^\circ$ . The  $\theta = 90^\circ$  spectrum exhibits the doublet structure characteristic of TTF-TCNQ, while the  $\theta = 15^\circ$  spectrum is dominated by the single peak at 399.9-eV binding energy ( $E_B$ ). Enhancement of this higher  $E_B$  peak is observed at  $\theta = 15^\circ$  when the crystals are mounted with the high-conductivity direction both perpendicular to and nearly parallel to the photoelectron take-off direction. Thus it is unlikely that an anisotropic,

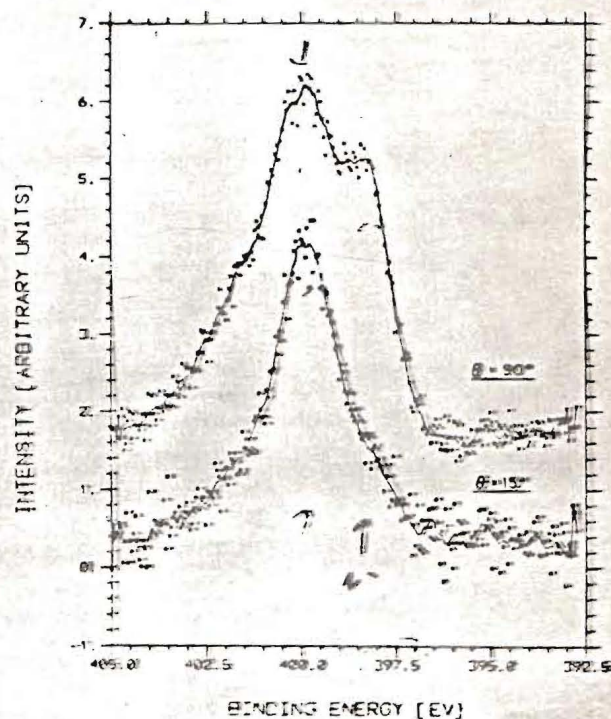


FIG. 2.  $N_{1s}$  grazing-angle spectra for TTF-TCNQ.

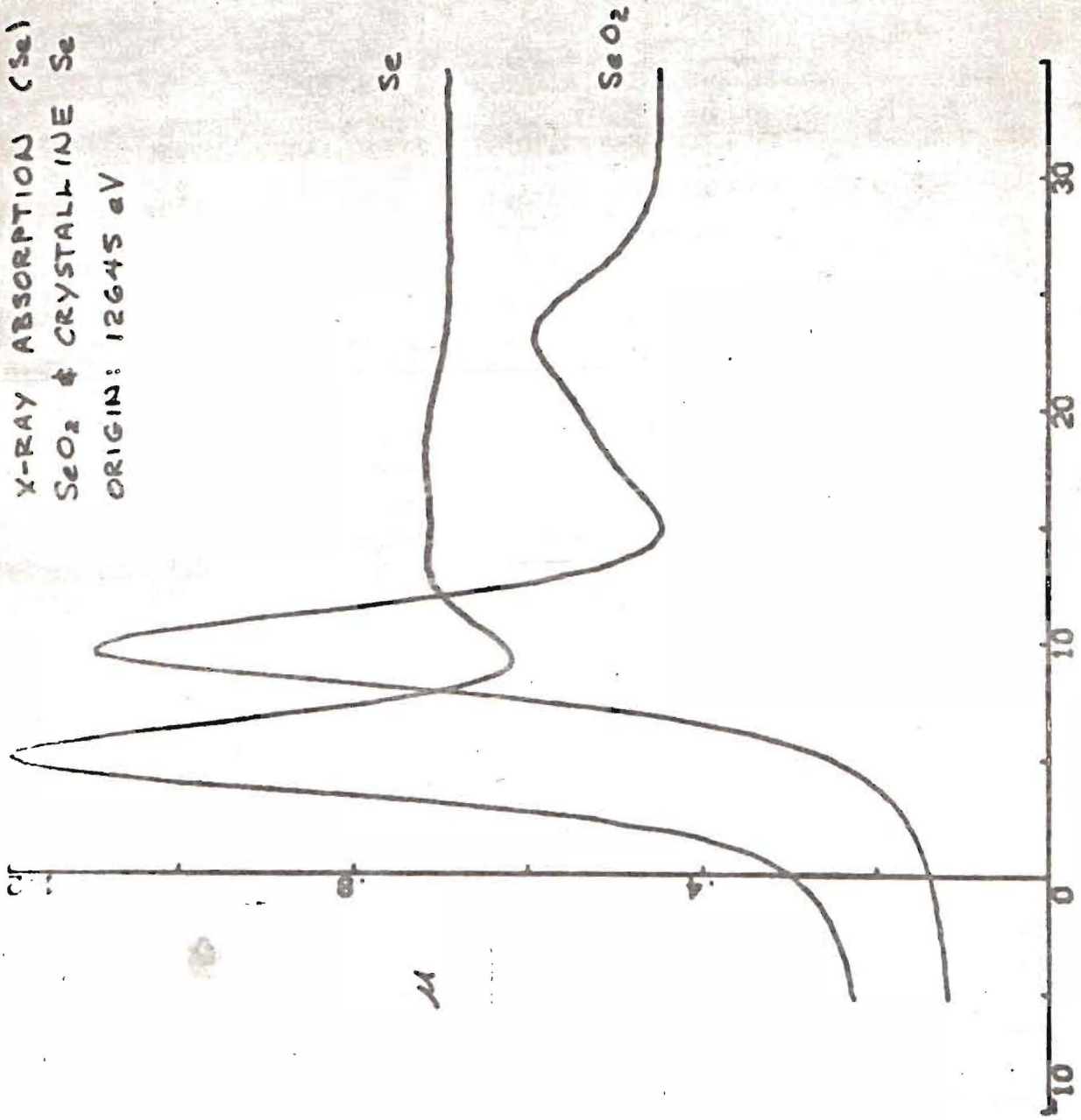
discrete energy loss with unit cross section in one direction could be responsible for the changes evident in Fig. 2.

Similar changes with  $\theta$  are also evident in the  $S_{2p}$  spectra. At  $\theta = 15^\circ$  the full width at half-maximum of the total  $S_{2p}$  envelope decreases by 0.3 to 0.5 eV and the position shifts by 0.2 to 0.4 eV toward lower  $E_B$ . These changes in the  $S_{2p}$  spectra are more subtle because the  $S_{2p}$  peak has a greater natural linewidth ( $\sim 0.5$  eV) because of spin-orbit coupling, and consequently the surface-bulk doublet is not as easily resolved. In addition, the kinetic energy of the  $S_{2p}$  photoelectron ( $\sim 1090$  eV) is 25% greater than that of the  $N_{1s}$  photoelectron ( $\sim 855$  eV) and the inelastic mean free path of the  $S_{2p}$  photoelectron ( $\lambda_{S_{2p}}$ ) will be greater than  $\lambda_{N_{1s}}$ .<sup>11</sup> This should result in relatively more bulk species contributing to the  $S_{2p}$  spectrum than to the  $N_{1s}$  spectrum, particularly at lower take-off angles.

Thus it appears that, at the  $a$ - $b$  surface, there is a thin layer of TTF-TCNQ which is distinguishable from the bulk. (This layer may or may not be present at the surfaces of other exposed crystal planes.) In order to ensure that our spectra were not impurity dominated, we sublimed away ca. 50% of our starting material by heating

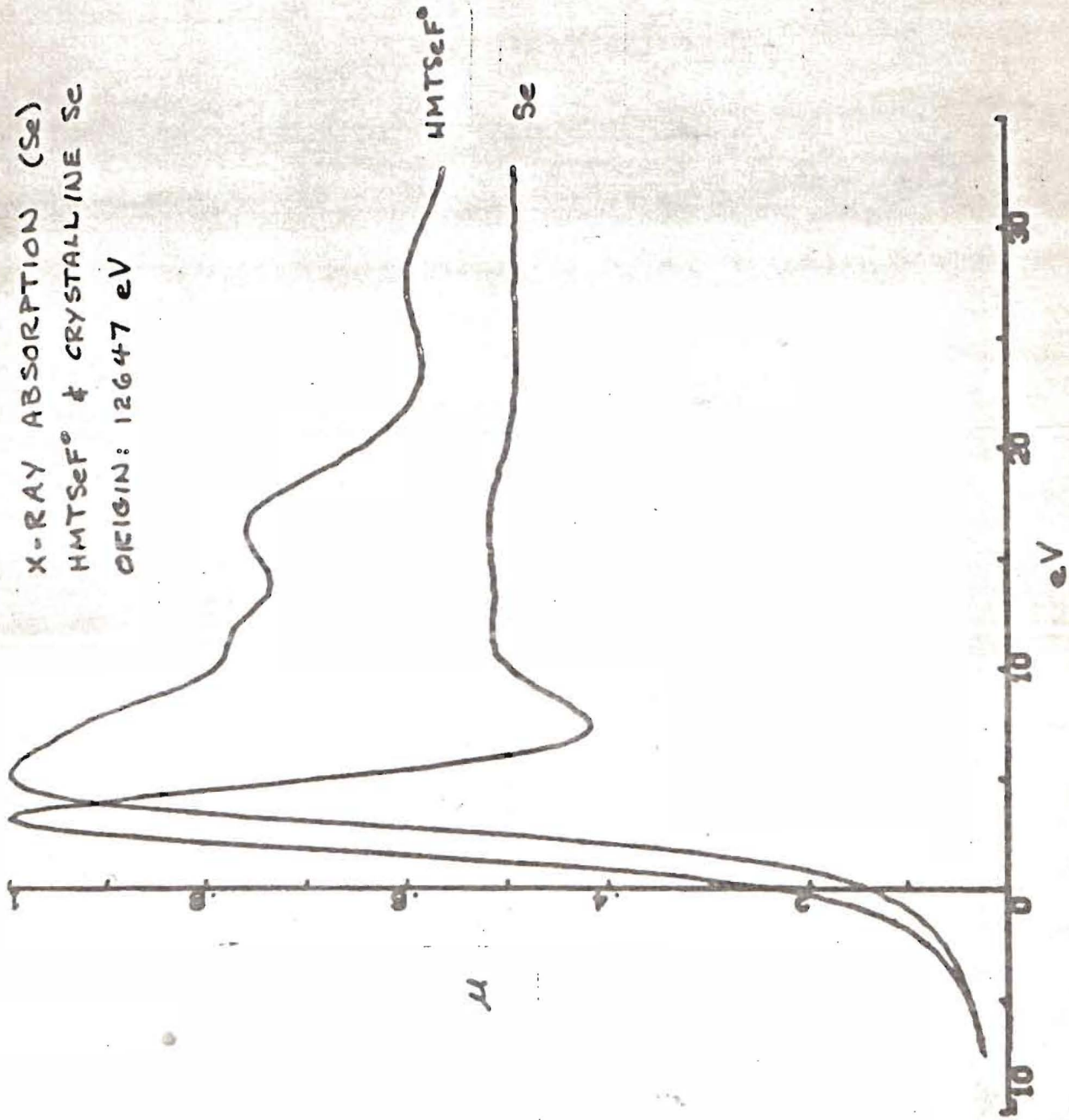


X-RAY ABSORPTION (Se)  
SeO<sub>2</sub> & CRYSTALLINE Se  
ORIGIN: 12645 eV



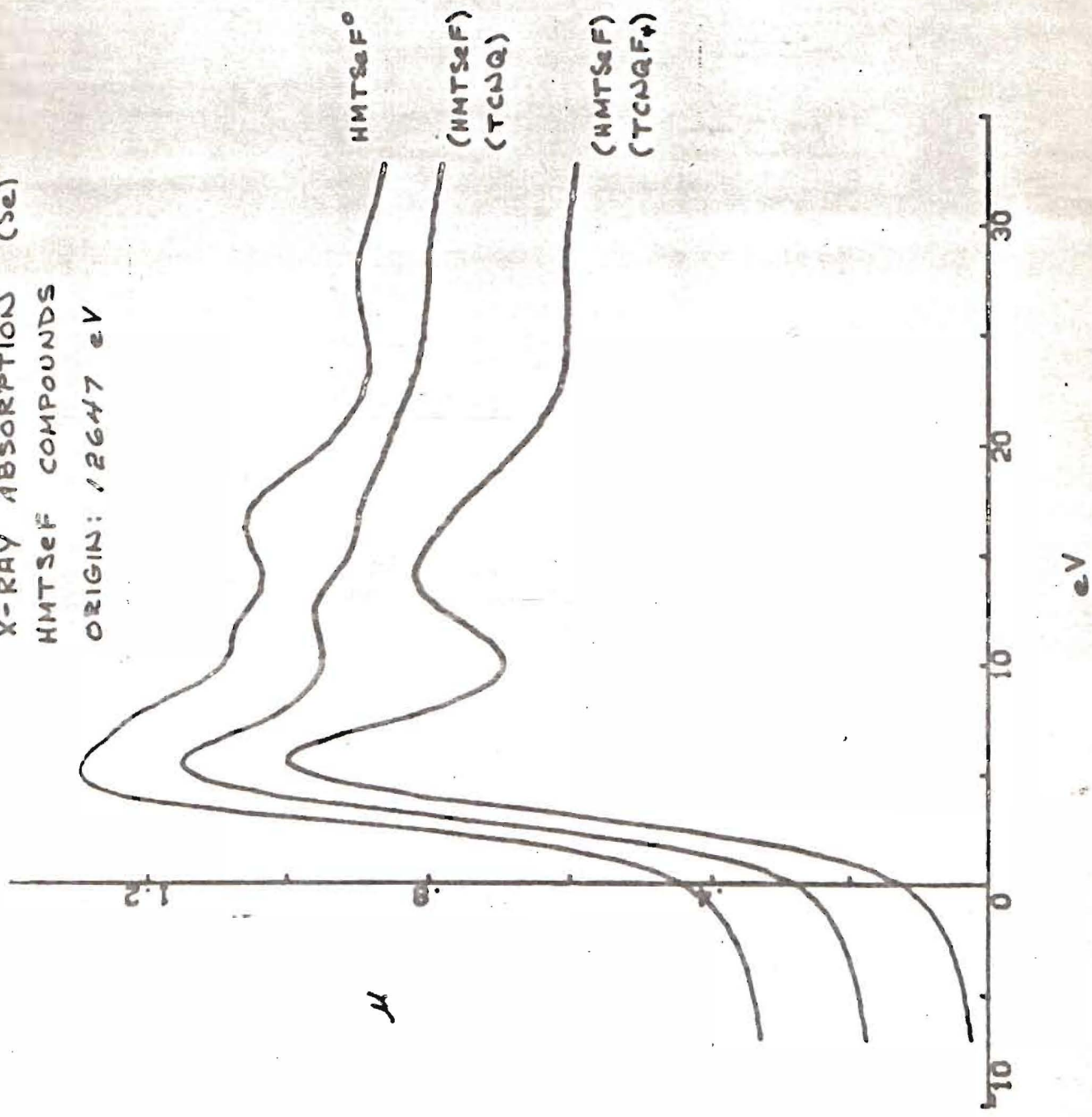


X-RAY ABSORPTION (Se)  
HMTSeF° & CRYSTALLINE Se  
ORIGIN: 12647 eV

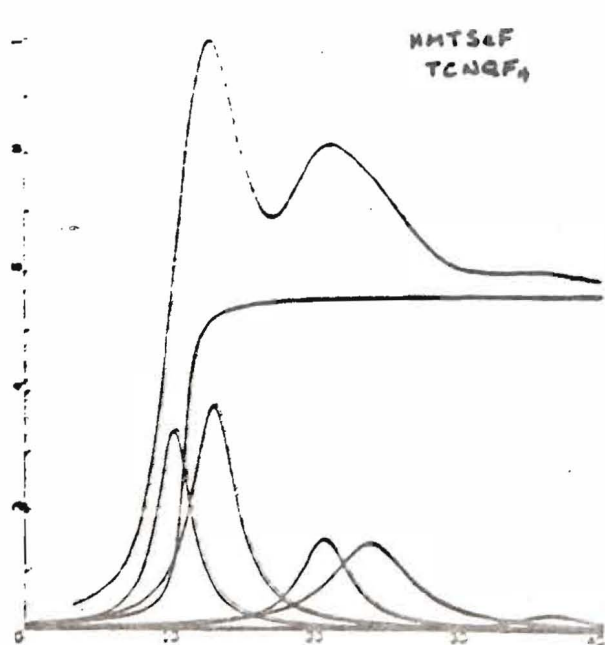
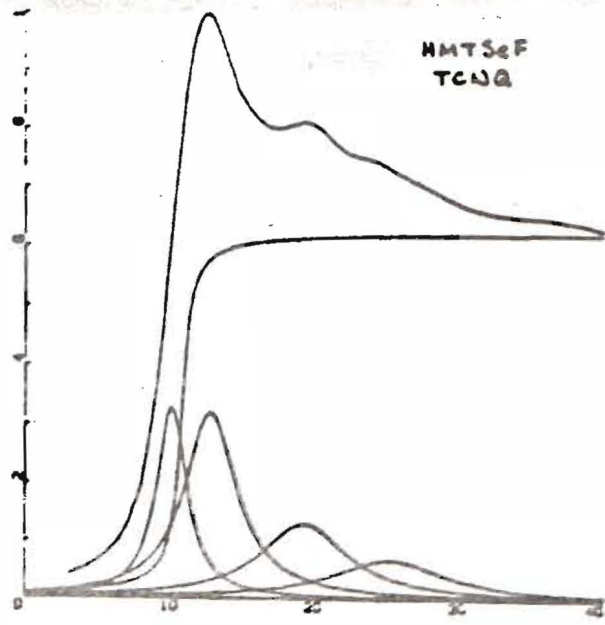
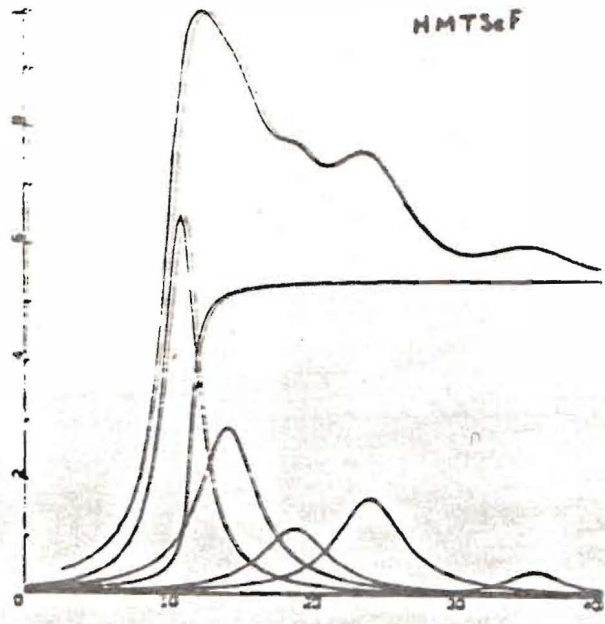




X-RAY ABSORPTION (Se)  
HMTSeF COMPOUNDS  
ORIGIN: 12647 eV









X-RAY ABSORPTION (Se)  
HMTSeF°, HMTSeF + MIXTURE  
ORIGIN: 12647 eV

